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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

24 April 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-087**  
Brent Viers (PRSM), "Thin Film Properties of POSS"

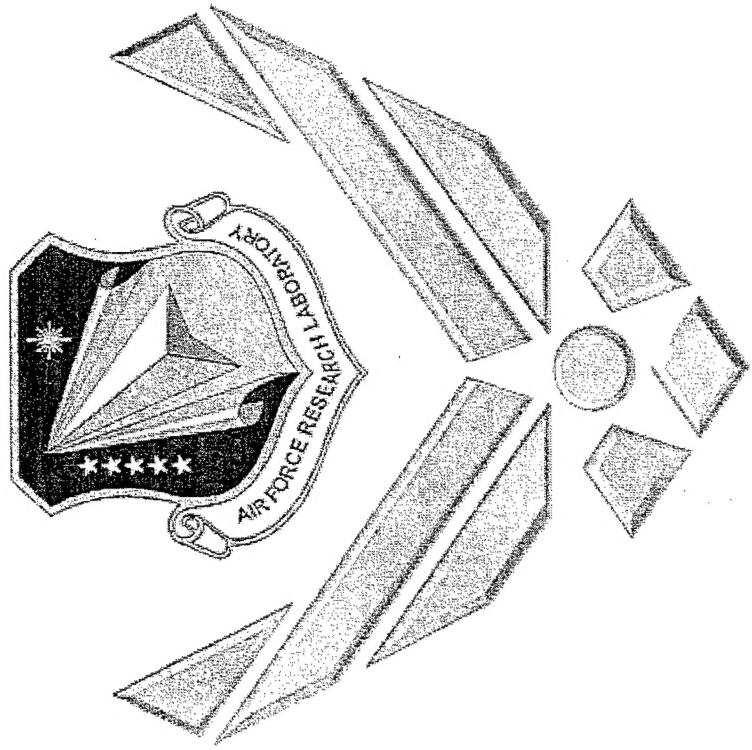
**SAMPE Presentation**

(Statement A)

(Long Beach, CA, 10-16 May 2002) (Deadline: 16 May 2002)

# Thin Film Properties of POSS

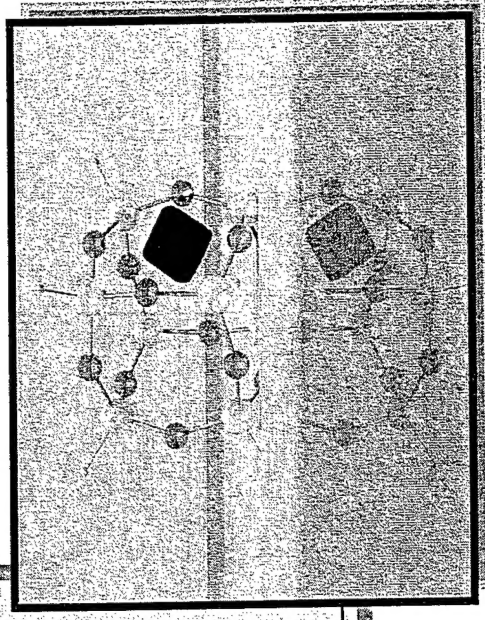
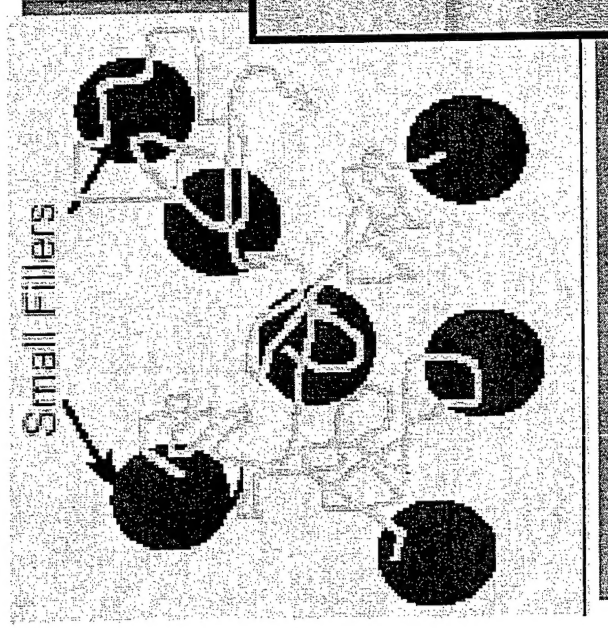
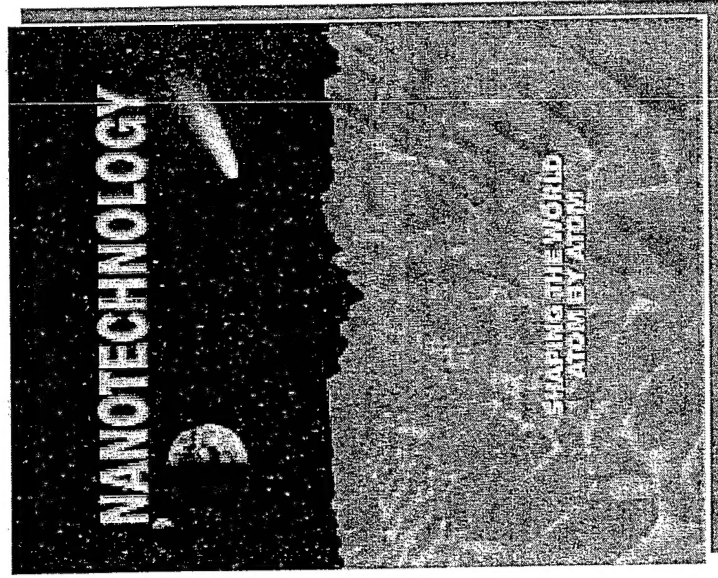
**DISTRIBUTION STATEMENT A**  
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Dr. Brent Viers  
POSS Polymer Group Leader  
Air Force Research Laboratory  
Propulsion Materials (AFRL/PRSM)  
Brent.viers@edwards.af.mil

# Inorganic-Organic Hybrids = Nanotechnology

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**“Perpetual Plastics:** By adorning the polymer structure of synthetic plastic with ceramic nanoparticles, researchers hope to develop new substances that will last far longer”

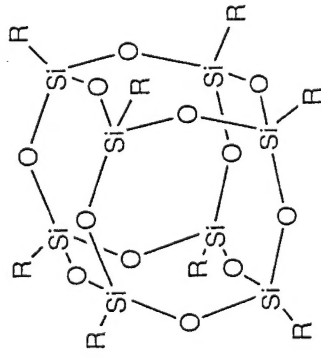
National Nanotechnology Initiative

<http://www.nano.gov>

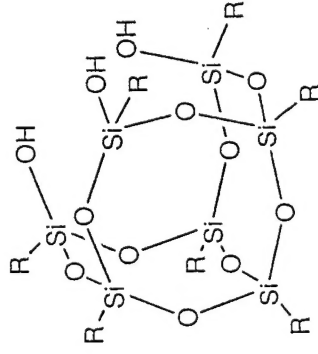
Mark Gordon, Iowa State U

# What is POSS?

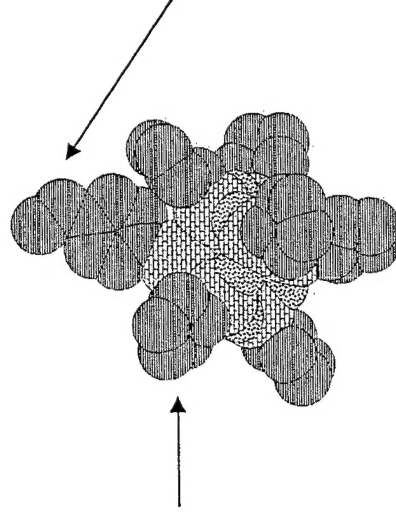
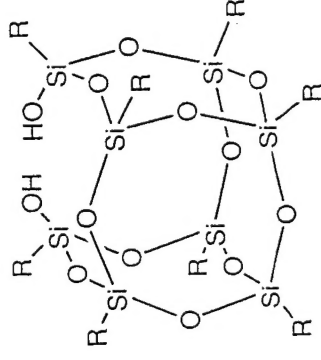
POSS=polyhedral oligomeric silsesquioxane



Nonreactive organic (R)  
groups for solubilization  
and compatibilization.



May possess one or more  
functional groups suitable for  
polymerization or grafting.

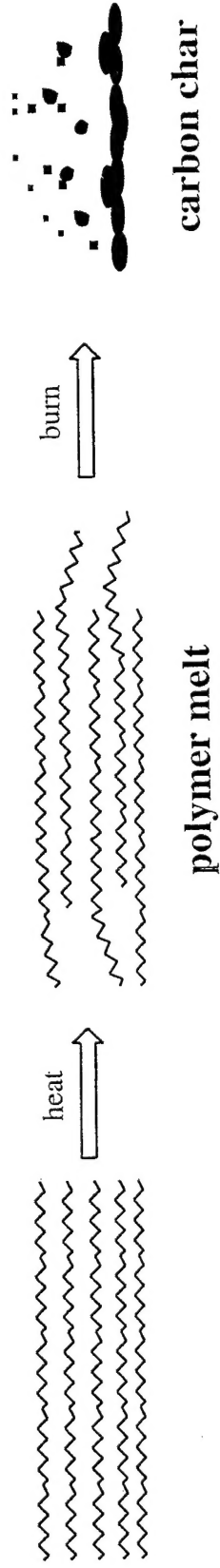


$$\text{Si} - \text{Si} = 5.4 \text{ \AA}$$

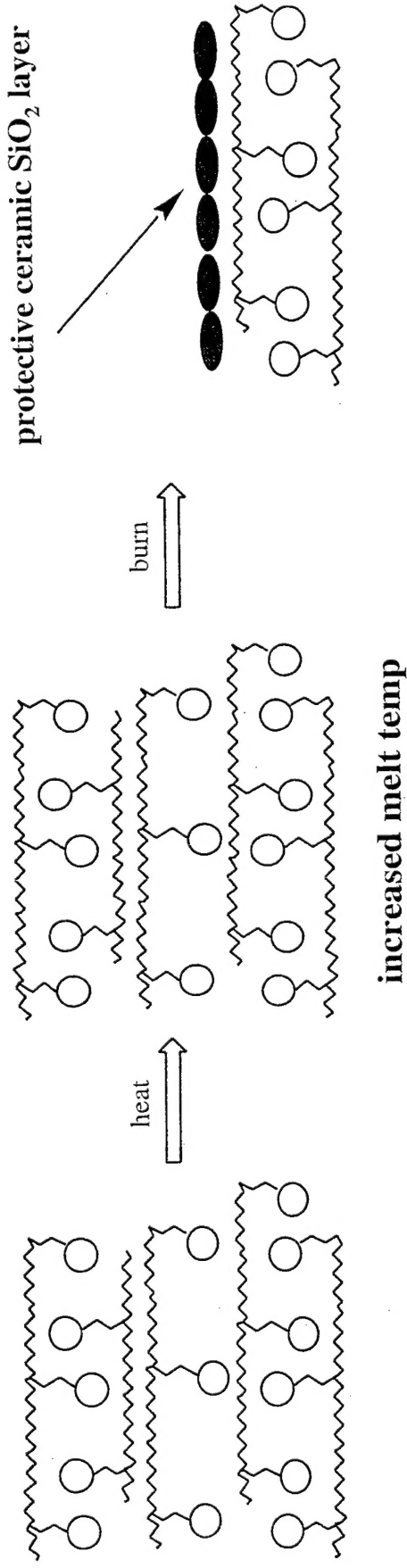
$$\text{Cp} - \text{Cp} = 15 \text{ \AA}$$

# POSS for Low Ablation Materials

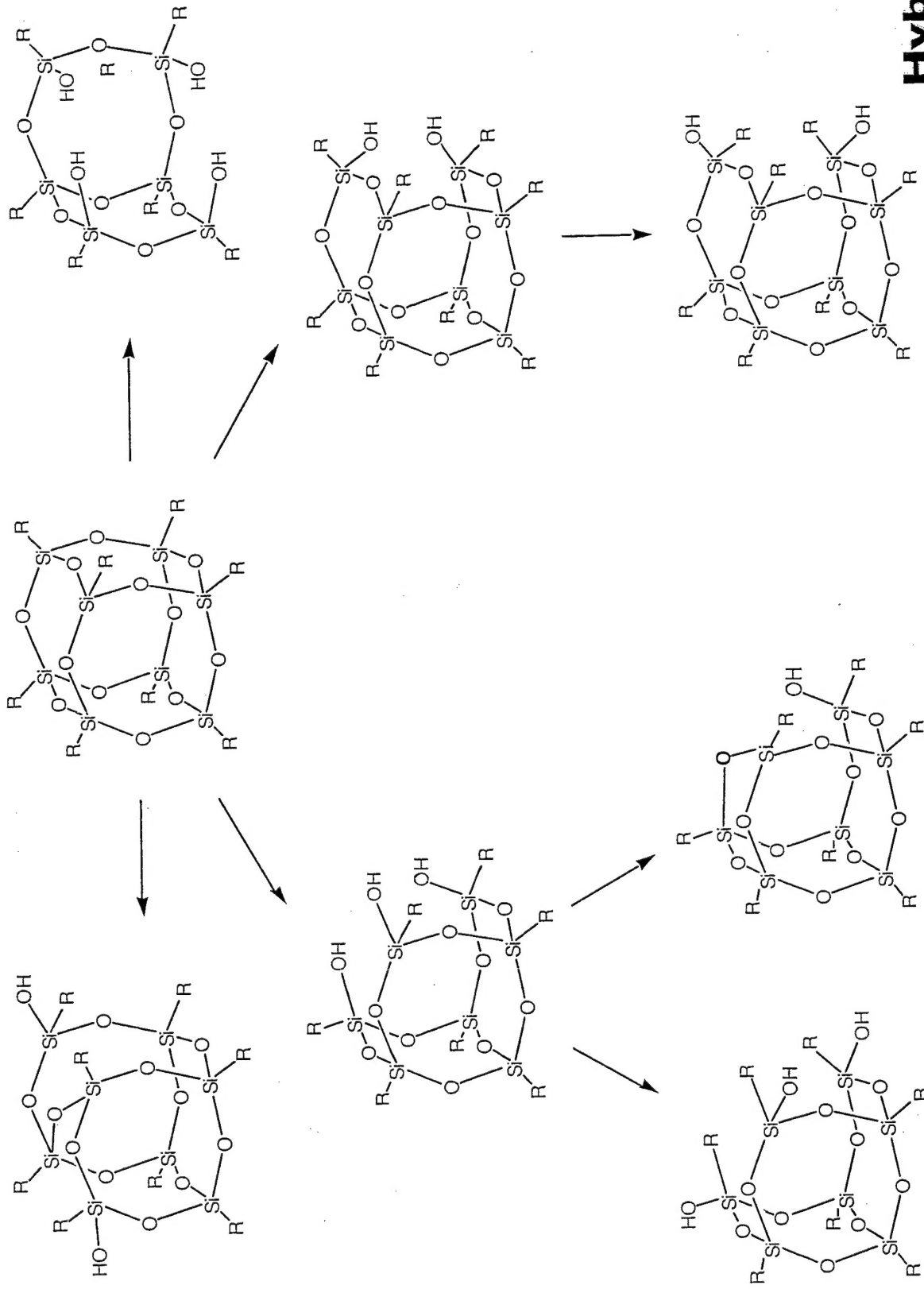
## Traditional Polymer



## POSS Polymer

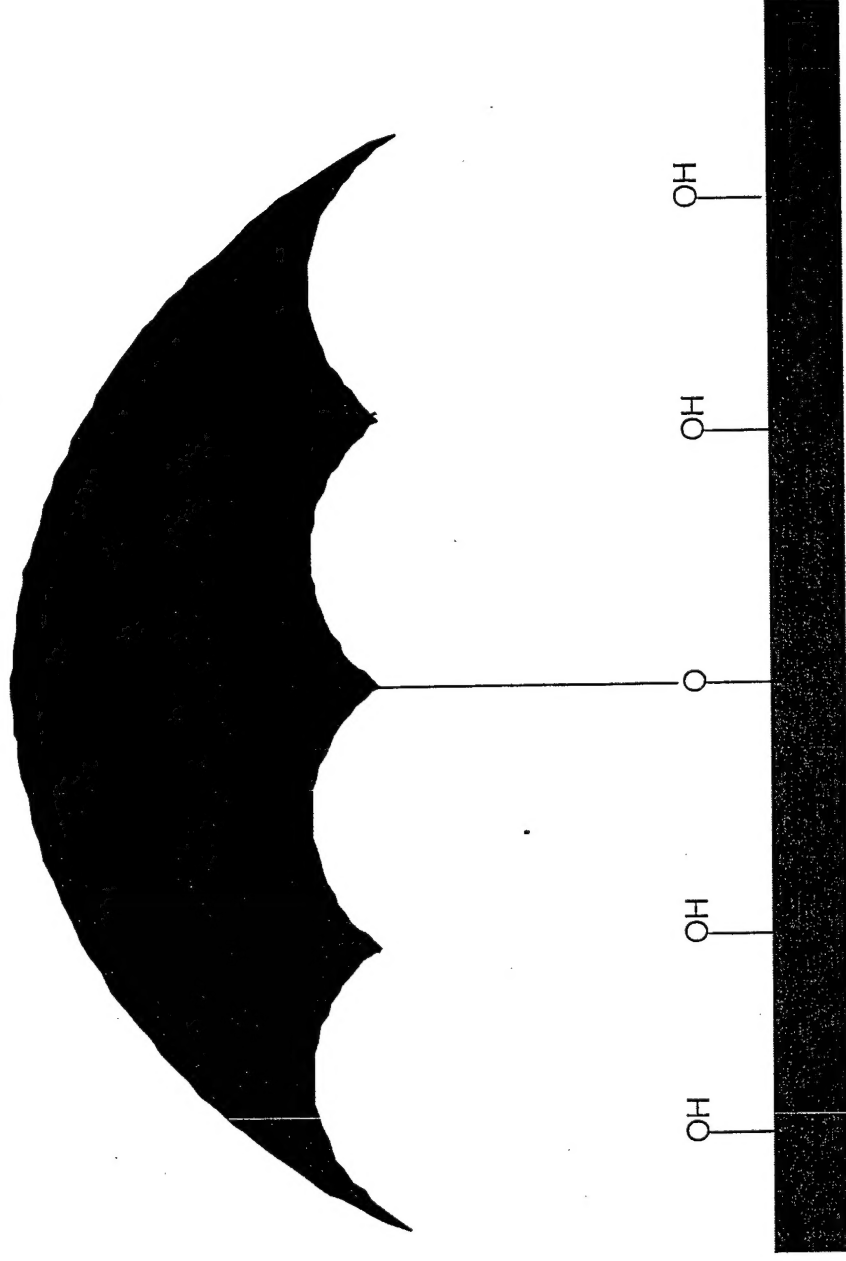


# Stereochemical and Topological Control



## POSS™: The Hydrophobic “Umbrella”

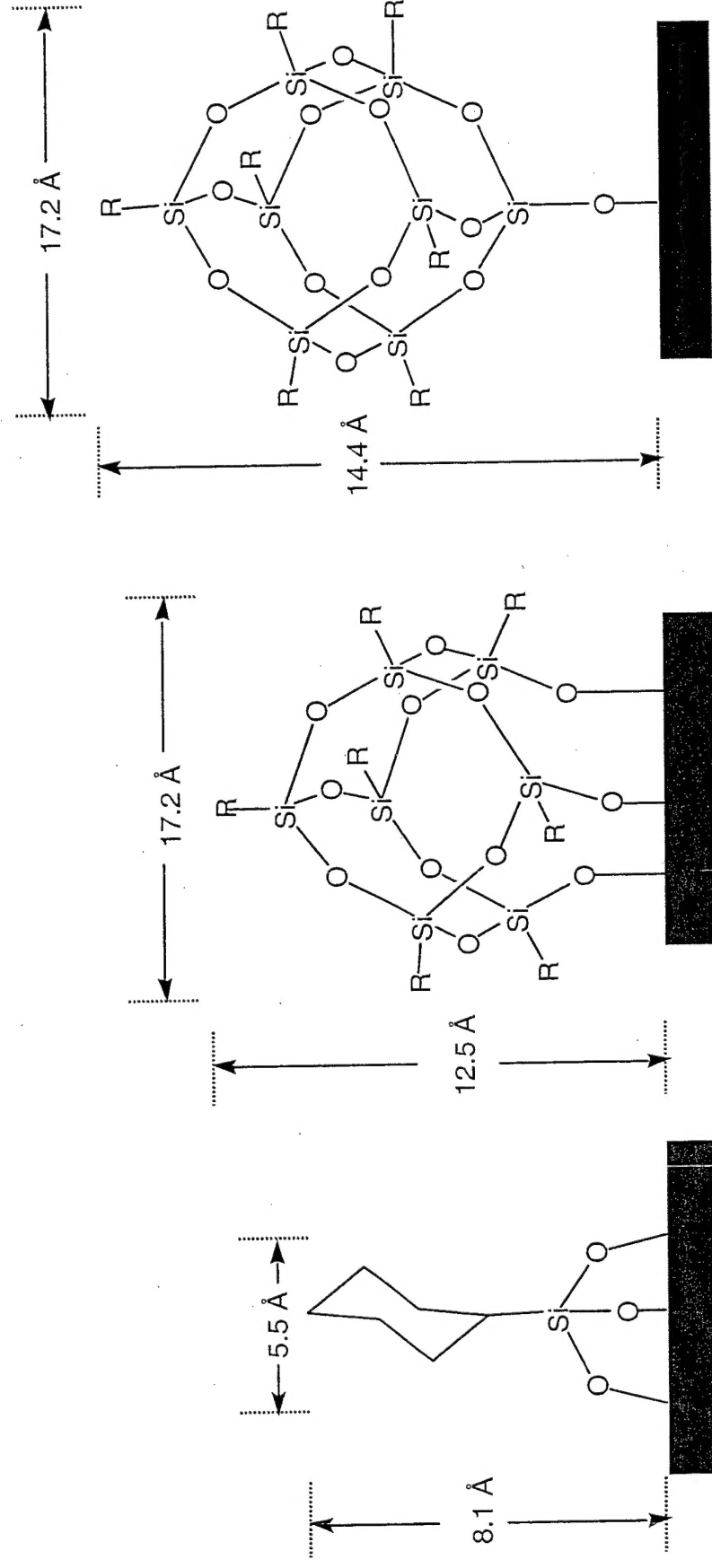
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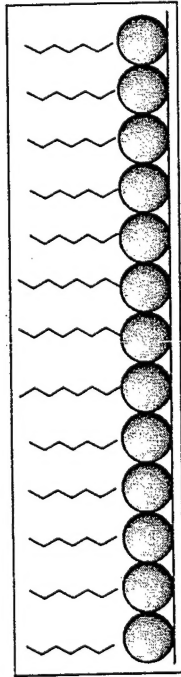
- POSS™ acts as a hydrophobic “umbrella” covering surface Si–OH groups (Approx. 10-12 Si–OH groups/POSS™ nanostructure)
- The surface coverage provided by a single POSS™ cage is approximately 8-10X that provided by a typical silane. (2.32 nm<sup>2</sup> vs. 0.24 nm<sup>2</sup>)



## Silanes vs. POSS™: Monolayer Comparison

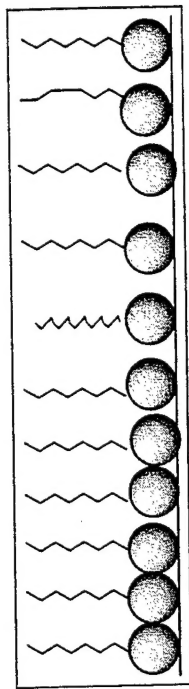


- The well-defined polyhedral structure leads to a more well-ordered, regular surface.
- POSS™ cages provide increased surface coverage leading to a more hydrophobic surface.



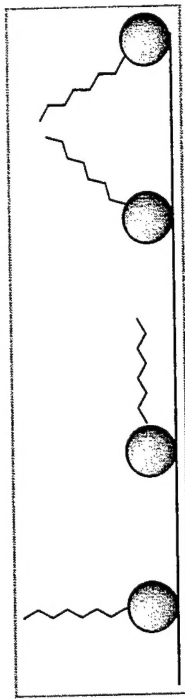
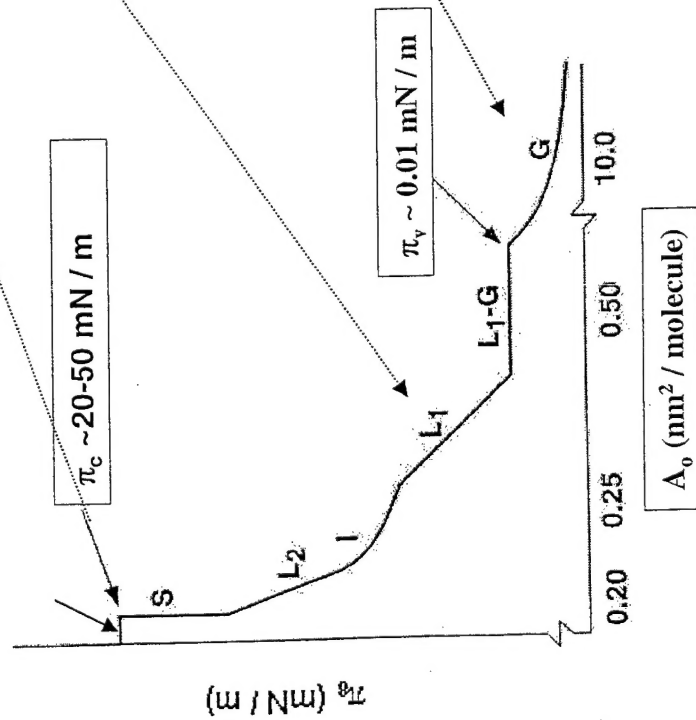
## Solid Phase

low compressibility ( $S$ ), nearly linear plot



## Liquid Phase

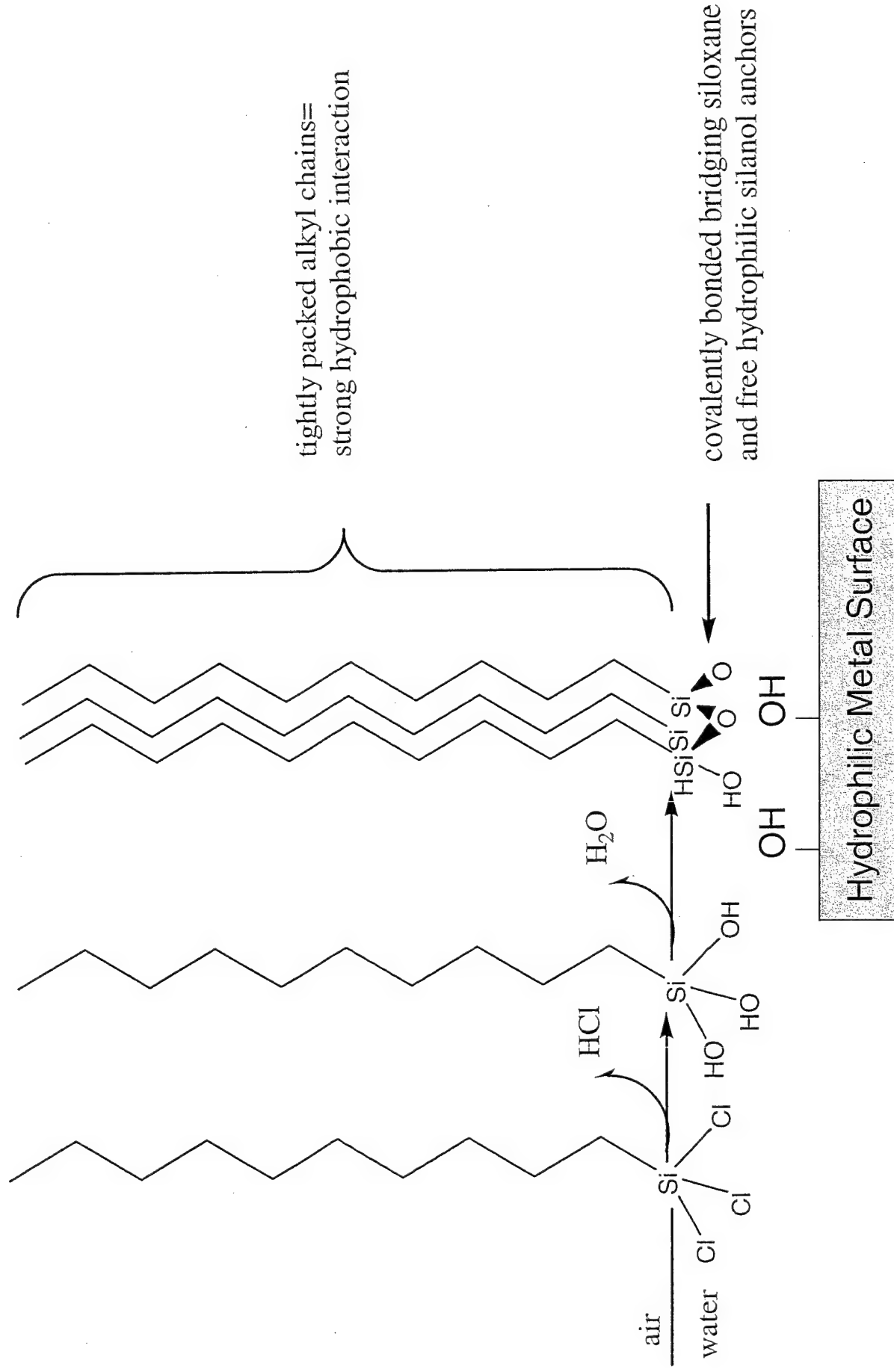
appear as liquid, some disorder in the structure, 2 types— liquid expanded ( $L_1$ ) and liquid condensed ( $L_2$ )



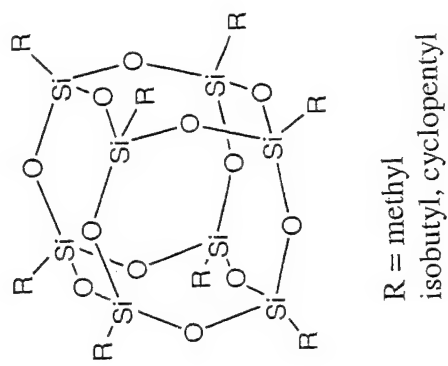
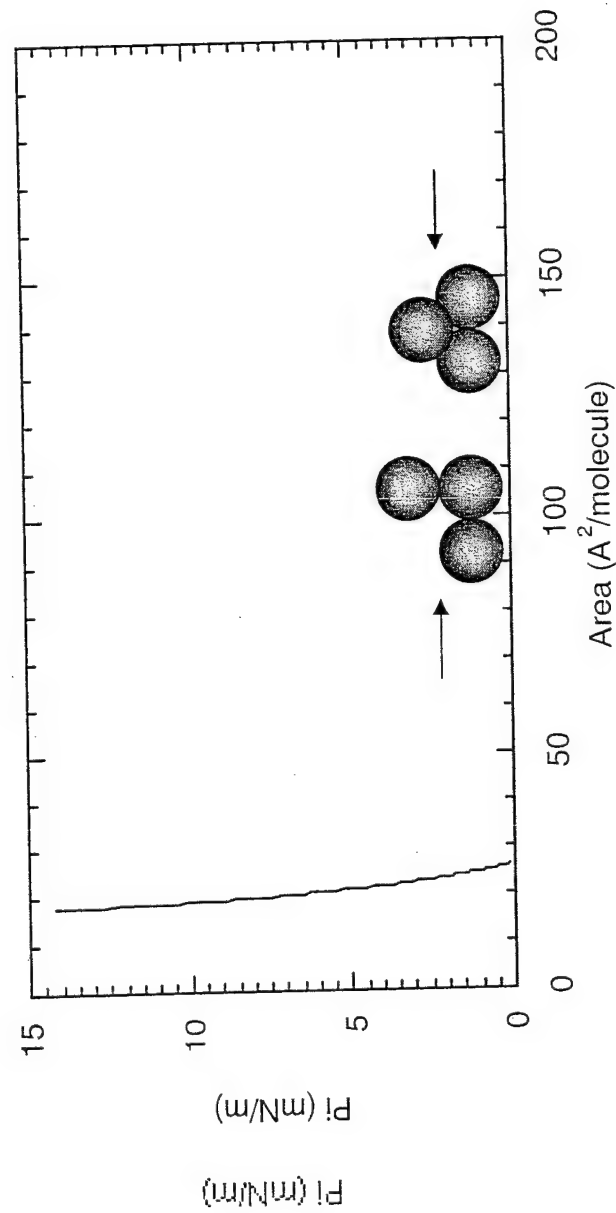
## Gas Phase

obey an equation of state,  $\Pi$  area per molecule is large,  $\Pi$  as low as 0.001 mN/m

# Chlorosilane Self Assembled Monolayers

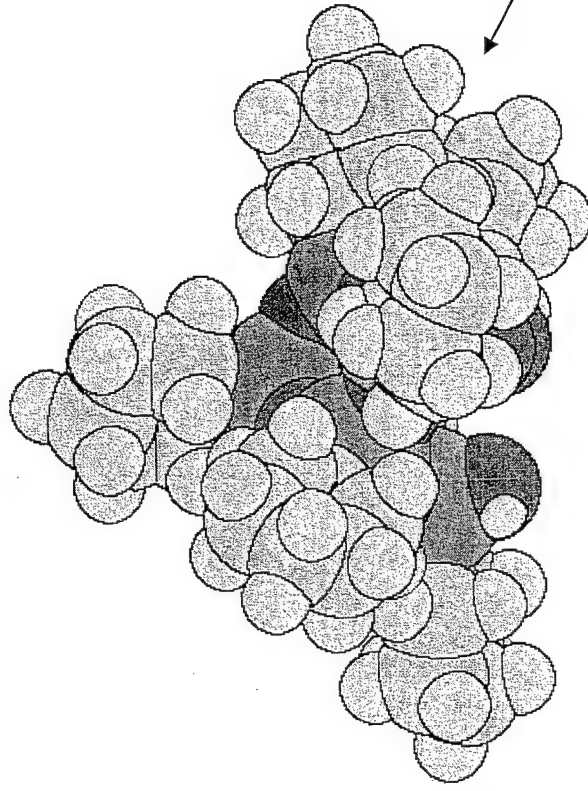


# Fully Condensed POSS Cubes



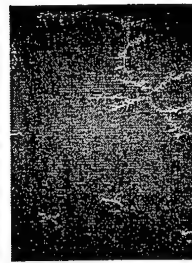
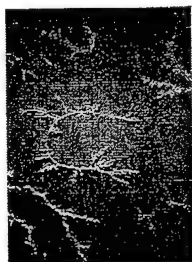
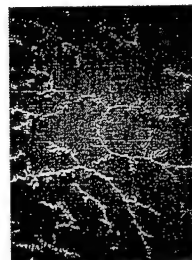
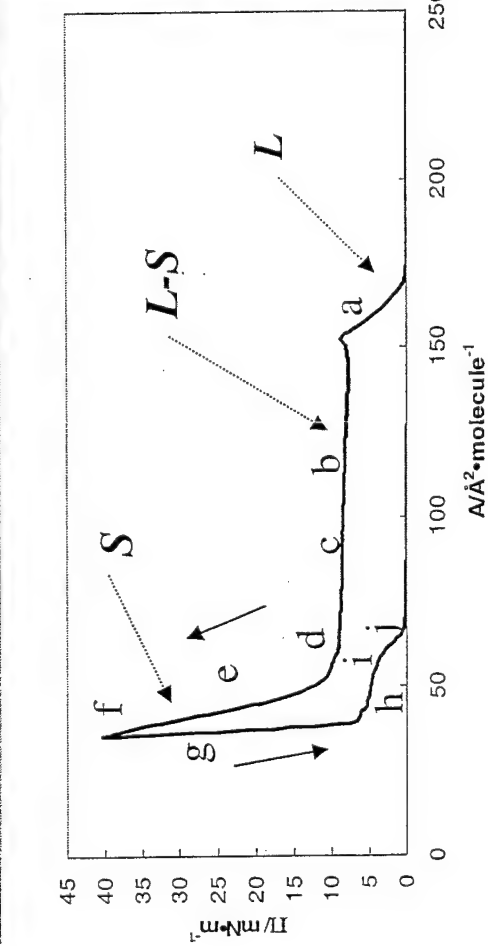
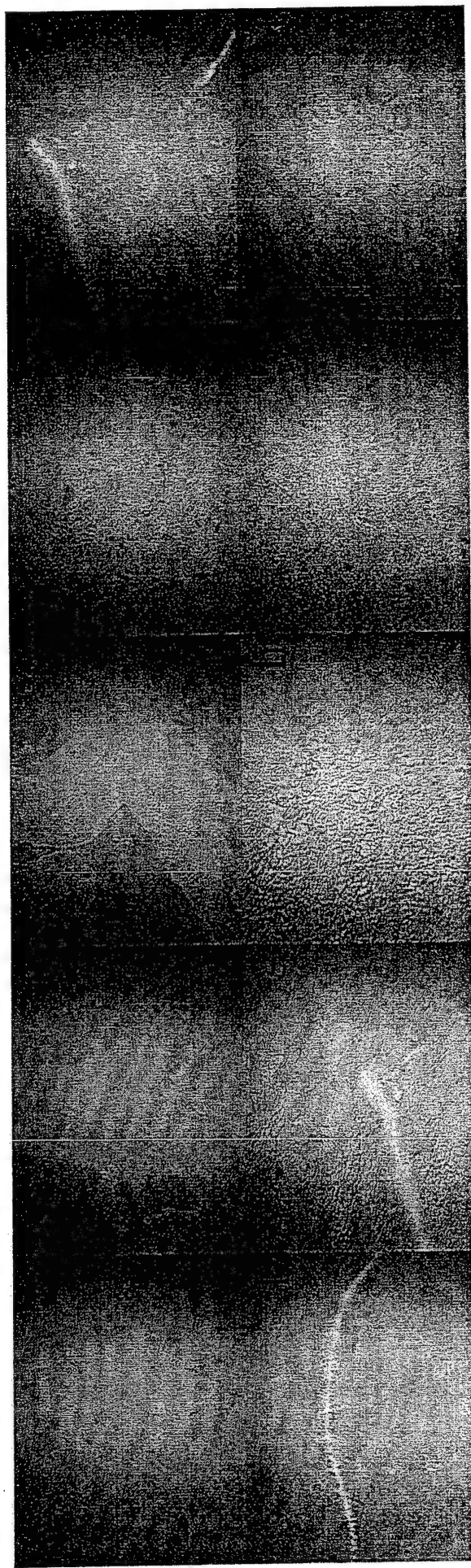
**POSS likely exists as aggregates that agglomerate upon compression**

## Steric Hindrance of POSS



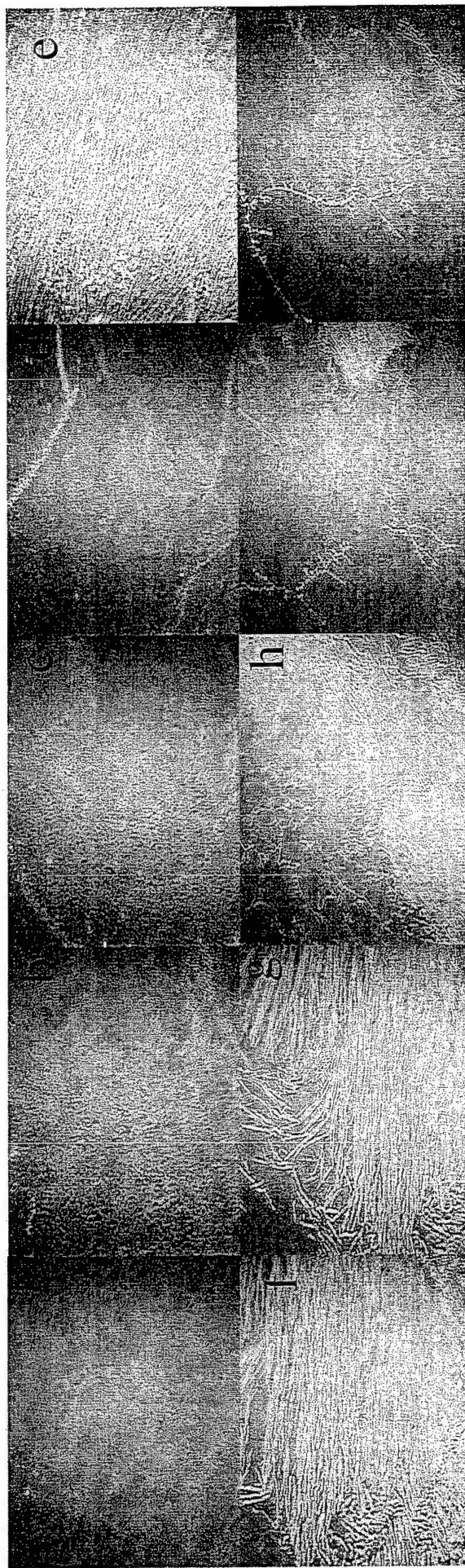
Hydrophobic  
Organic groups  
Extend past  
Hydrophilic  
Silanols!

# Cyclopentyltrisilanol-POSS @ 22.5 °C

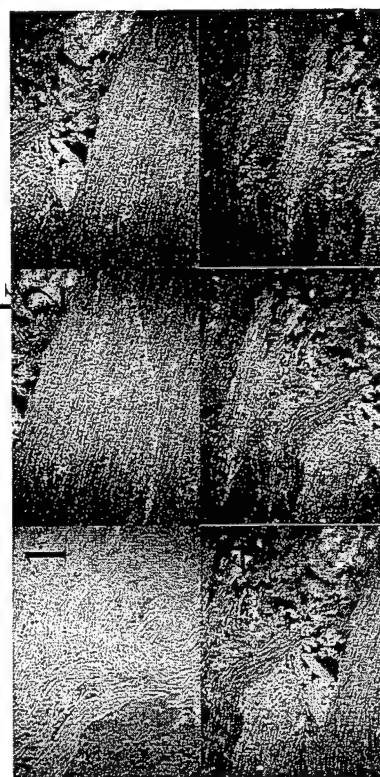


250 1-6 ,dendritic structures obtained during expansion in a second compression/expansion cycle

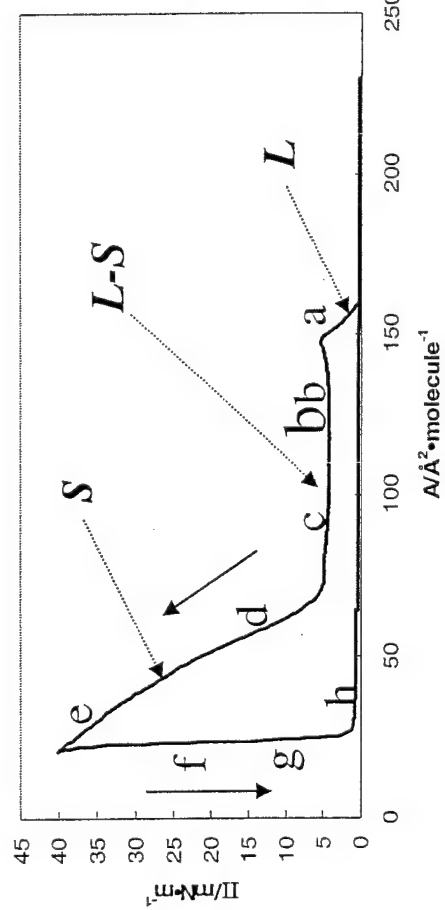
# Cyclohexyltrisilanol-POSS @ 22.5°C



I

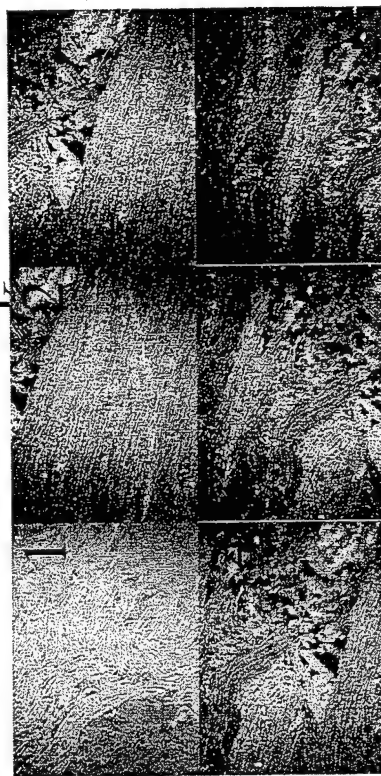
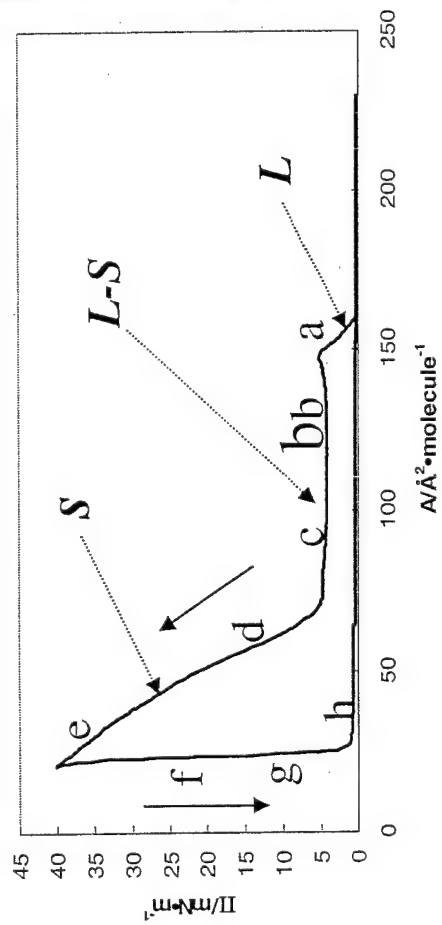
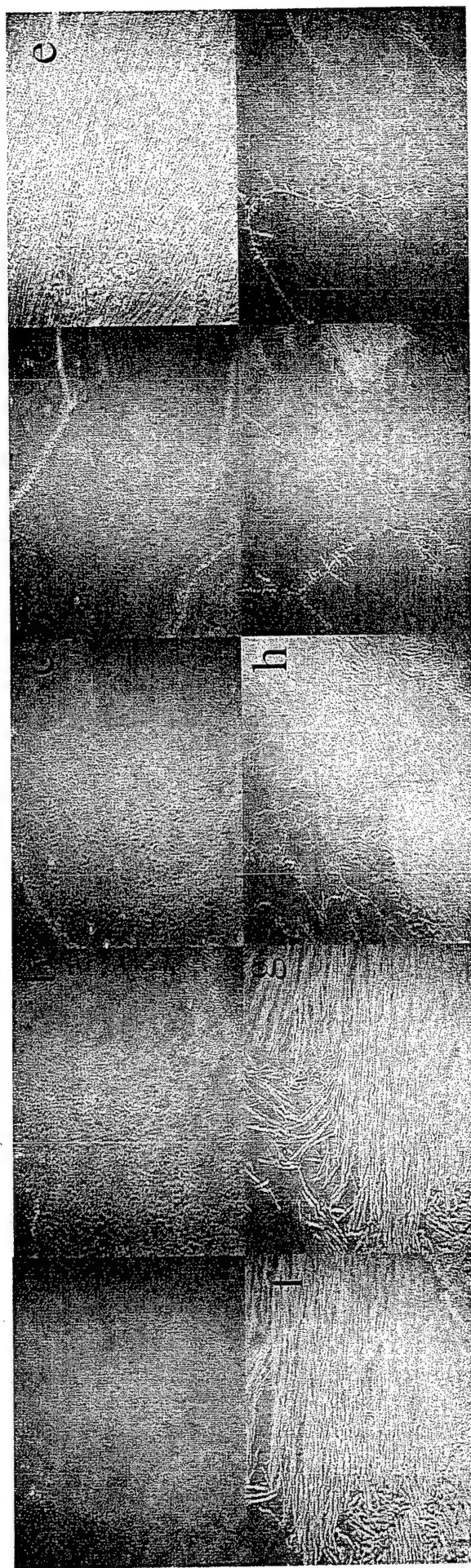


1-6 show the solid state film during 2<sup>nd</sup> compression





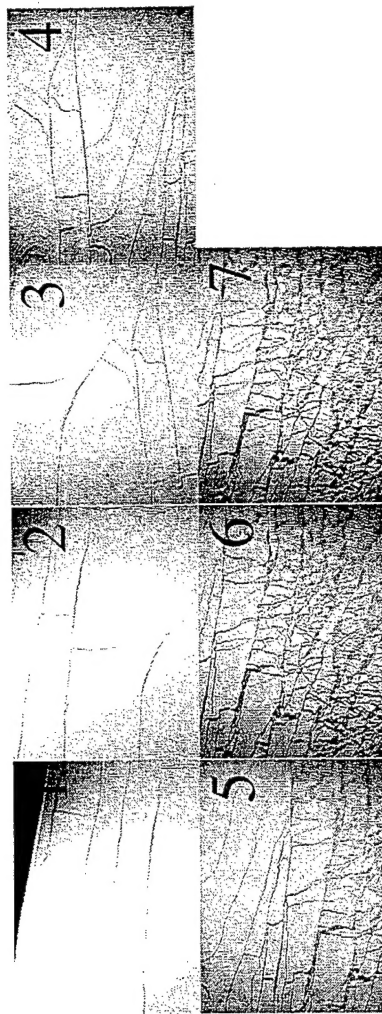
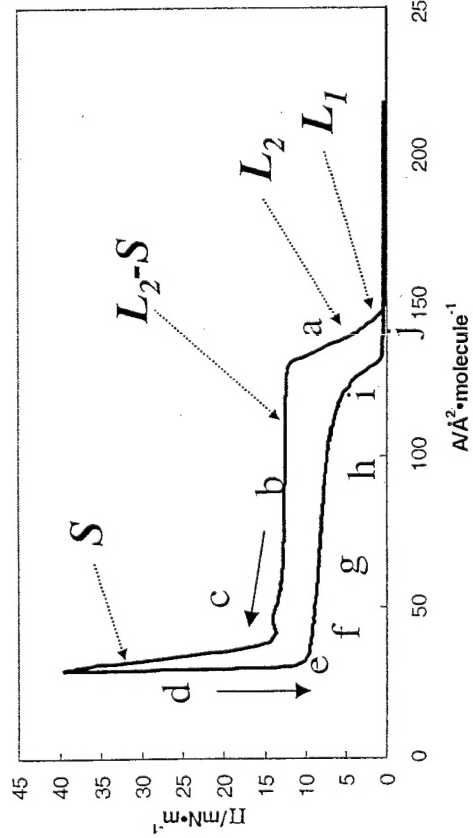
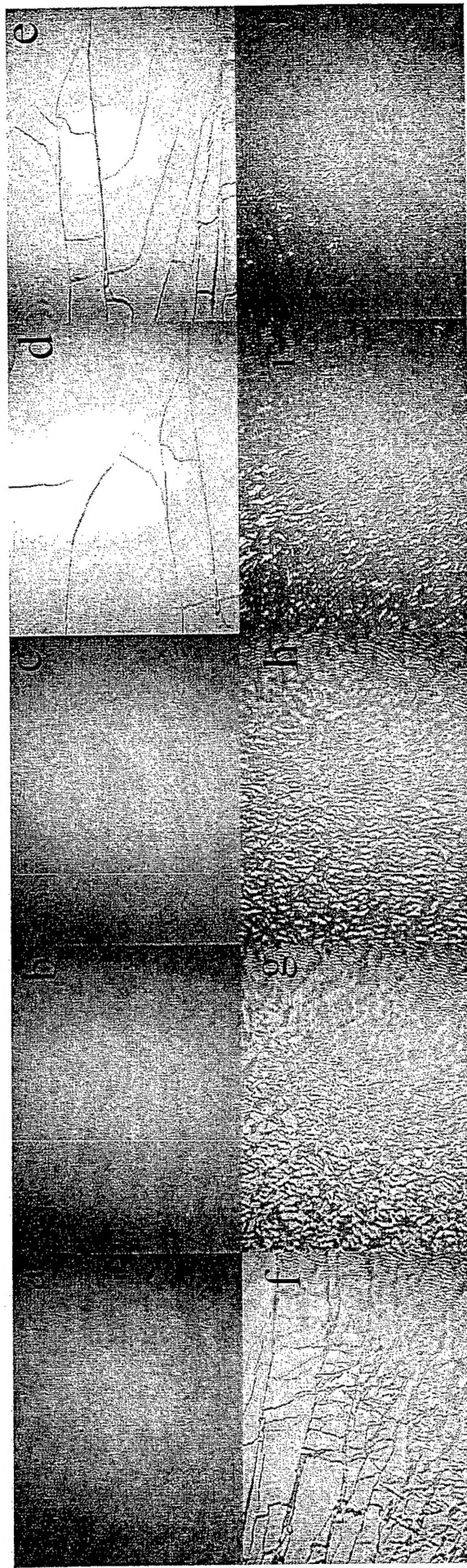
# Cyclohexyltrisilanol-POSS @ 22.5°C



1-6 show the solid state film during 2<sup>nd</sup> compression



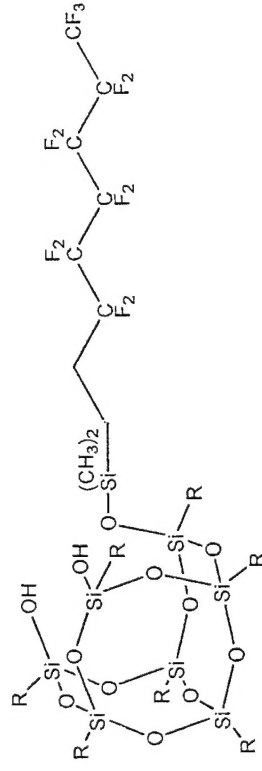
# Phenyltrisilanol-POSS @ 22.5°C



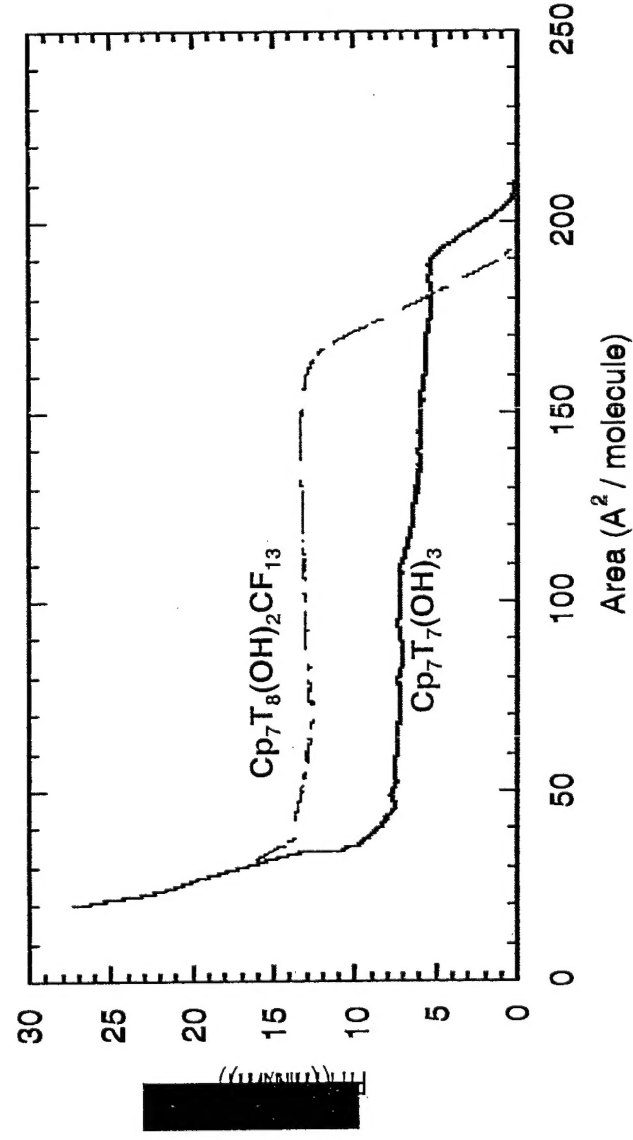
1-7 show the early details of solid state film break-up upon expansion

# POSS in a "traditional" surfactant

Quantitative substitution of first silanol



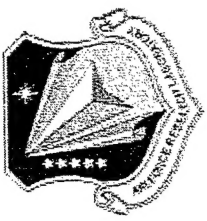
R = cyclopentyl



Pressure-Area behavior is very similar to POSS precursor

## Conclusions

- POSS with hydrophilic silanol groups can spread to form monolayers on a water surface
- Different POSS geometries (functionality) can change the compression behavior in a Langmuir Blodgett apparatus
- POSS surfactants can have complicated collapse behavior which likely affects the filler behavior (vis a vis aggregation effects)
- Transfer experiments are underway



## Acknowledgments

- POSS group at AFRL-Edwards (Shawn Phillips, Rusty Blanski, Tim Haddad, Brian Moore, Justin Leland, Pat Ruth, Capt. Rene Gonzalez, Maj. Steve Svejda)
- Hybrid plastics (Joe Lichtenhan, Joe Schwab, Bill Reinerth)
- AFOSR (Dr. Charles Lee), Edwards AFRL-propulsion directorate